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(54) **Organic electroluminescent devices with improved stability and efficiency**

Organische elektrolumineszente Vorrichtungen mit verbesserter Stabilität und Effizienz

Dispositif organique électroluminescent à stabilité et efficacité améliorée

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(56) References cited:
WO-A-99/53724

US-A- 5 601 903

- **Y. HAMADA ET AL.: "Red organic light-emitting diodes using an emitting assist dopant"**
APPLIED PHYS. LETT., vol. 75, no. 12, 20
September 1999 (1999-09-20), pages 1682-1684,
XP002196211
- **FATEMI D J ET AL: "HIGHLY FLUORESCENT MOLECULAR ORGANIC COMPOSITES FOR LIGHT-EMITTING DIODES" SYNTHETIC METALS, ELSEVIER SEQUOIA, LAUSANNE, CH,**
vol. 85, 1997, pages 1225-1228, XP002911748
ISSN: 0379-6779
- **HAMADA Y ET AL: "INFLUENCE OF THE EMISSION SITE ON THE RUNNING DURABILITY OF ORGANIC ELECTROLUMINESCENT DEVICES" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP,**
vol. 34, no. PART 2, 1 July 1995 (1995-07-01),
pages 824-826, XP002061754 ISSN: 0021-4922

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Description

[0001] The present invention relates to organic electroluminescent devices and more particularly to an emission layer with suitable dopants for improving operational stability and efficiency of these devices.

5 [0002] An OLED device includes a substrate, an anode, a hole-transporting layer made of an organic compound, an organic luminescent layer with suitable dopants, an organic electron transport layer, and a cathode. EL devices are attractive because of their low driving voltage, high luminance, wide-angle viewing and capability for full-color flat emission displays. Tang and others. described this multilayer EL device in their commonly assigned US-A-4,769,292 and US-A-4,885,211.

10 [0003] The following patents and publications disclose the preparation of EL devices with improved operational life-time. Structure modifications, stable cathode and confinement of carriers and their recombination in the emission zone achieved significant improvement in the operation stability of these devices. So and others. discussed an EL device in US-A-5,853,905 consisting of a single organic emission layer with a mixture of electron transport and hole transport material, sandwiched between anode and cathode. However, this device has low efficiency.

15 [0004] Popovic and others. described an EL device in SPIE Conference proceedings Vol. 3476, p. 68-72, 1998 with improved efficiency and stability by mixing emitting electron transport material and the hole transport material. Chen and others. reported a highly efficient red color device where Alq emission layer is doped with DCJTb. (US-A-5,908,581 and Micromol. Symp. 25, 490 (1997)).

20 [0005] Hamada and others. reported in Applied Phys. Lett. 75,1682 (1999) a red EL device by doping rubrene and DCM₂ dopants into Alq emission layer. With the prospect of using these EL devices in display screens for laptop computers, digital personal organizers, cellular phone and so forth, there is a need for EL device with much stable operation for luminance and driving voltage.

[0006] Forrest and others disclosed in WO 9 953 724 an EL device including a mixture of hole transport materials as Alq₃ with TPD and DCM₂ as dopant.

25 [0007] It is therefore an object of the present invention to provide an EL device with improved operational stability and luminance efficiency.

[0008] This object is achieved by an organic luminescent layer for use in an electroluminescent device with improved operating life, comprising:

- 30 a) an organic host material capable of sustaining both hole and electron injection and recombination; and
b) at least three dopants:

- 35 i) a first dopant capable of accepting energy of electron-hole combinations in the host material; and
ii) a second dopant capable of trapping the holes from the host material; and
iii) a third dopant capable of accepting energy from the electron hole combination in the host material and accepting energy transferred from the second dopant;

c) the first dopant being selected so that the bandgap energy of the first dopant is less than the bandgap energy of the host material; and

40 d) the second dopant being selected to have a hole trapping energy level above the valance band of the host material.

[0009] A feature of the present invention is that by properly selecting the first and second dopants, the operating life of an electroluminescent device incorporating the electroluminescent layer can be significantly improved.

45 [0010] Another feature of the invention is that it can be used to provide an electroluminescent device with improved chromaticity.

[0011] Another feature of the invention is that it can be used to provide an electroluminescent device with improved operational stability at high luminance output.

[0012] Another feature of the invention is that it can be used with a low voltage drive source.

50 [0013] Quite unexpectedly, it has been found in this invention that synergetic effect of doping exciton trapping dopant and hole trapping dopant was such that better operational stability and efficiency were obtained at lower concentrations of the dopants. This resulted in improvements in operating lifetime and luminance efficiency. With an additional third luminescent dopant for controlling the color of the emission, excellent color chromicity was obtained, which could not be achieved with any other combination.

55 [0014] The devices made in accordance with the present invention are highly stable and have excellent luminance properties.

FIG. 1 is simple structure of an organic light-emitting device;

FIG. 2 is a schematic diagram of an organic light-emitting device in which a light-emitting structure is deposited over an ITO anode with an emission layer prepared according to the present invention;

FIG. 3 shows a graphic representation of the energy level diagram of the Alq host, exciton trapping dopant (EXD) (dopant 1), hole trapping dopant (HD) (dopant 2) and luminescent dopant (LD) (dopant 3) in the emission layer;

FIG. 4 shows the relative normalized operational luminance as a function of operation time for doped EL devices;

FIG. 5 shows the relative driving voltage as a function of operation time for the EL devices of FIG. 4;

FIG. 6 shows the relative normalized luminance as a function of operation time for doped EL devices; and

FIG. 7 shows the relative driving voltage as a function of operation time for the EL devices of FIG. 6.

[0015] The drawings are necessarily of a schematic nature, since the thicknesses of the individual layers are too thin and thickness differences of the various elements too great to permit depiction to scale or to permit convenient proportionate scaling.

[0016] The light-emitting layer of the organic EL device comprises a luminescent or fluorescent material where electroluminescence is produced as a result of electron-hole pair recombination in this region. In the simplest construction, as shown in FIG. 1, the light-emitting layer 108 is sandwiched between anode 104 and cathode 106. The light-emitting layer is a pure material with a high luminescent efficiency. A well known material is tris (8-quinolinato) aluminum, (Alq), which produces excellent green electroluminescence.

[0017] The simple structure 100 can be modified to a three-layer structure as shown in FIG. 2, in which an additional electroluminescent layer is introduced between the hole and electron-transporting layers to function primarily as the site for hole-electron recombination and thus electroluminescence. In this respect, the functions of the individual organic layers are distinct and can therefore be optimized independently. Thus, the electroluminescent or recombination layer can be chosen to have a desirable EL color as well as high luminance efficiency. Likewise, the electron and hole transport layers can be optimized primarily for the carrier transport property.

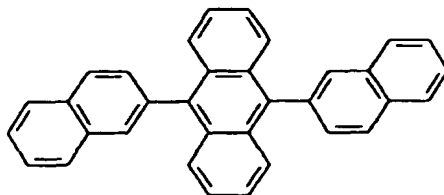
[0018] Turning to FIG. 2, a multilayer organic light-emitting device 200 has a light-transmissive substrate 202 on which is disposed a light-transmissive anode 204. The anode 204 comprises two layers 204a and 204b. An organic light-emitting structure 208 is formed between the anode 204 and a cathode 206. The organic light-emitting structure 208 is comprised of, in sequence, an organic hole-transporting layer 210, an organic light-emitting layer 212, and an organic electron-transporting layer 214. When an electrical potential difference (not shown) is applied between the anode 204 and the cathode 206, the cathode will inject electrons into the electron-transporting layer 214, and the electrons will migrate across layer 214 to the light-emitting layer 212. At the same time, holes will be injected from the anode 204 into the hole-transporting layer 210. The holes will migrate across layer 210 and recombine with electrons at or near a junction formed between the hole-transporting layer 210 and the light-emitting layer 212. When a migrating electron drops from its conduction band to a valance band in filling a hole, energy is released as light, and is emitted through the light-transmissive anode 204 and substrate 202.

[0019] The organic EL devices can be viewed as a diode, which is forward biased when the anode is at a higher potential than the cathode. The anode and cathode of the organic EL device can each take any convenient conventional form, such as any of the various forms disclosed by Tang and others. US-A-4,885,211. Operating voltage can be substantially reduced when using a low-work function cathode and a high-work function anode. The preferred cathodes are those constructed of a combination of a metal having a work function less than 4.0 eV and one other metal, preferably a metal having a work function greater than 4.0 eV. The Mg: Ag of Tang and others. US-A-4,885,211 constitutes one preferred cathode construction. The Al:Mg cathodes of Vanslyke and others. US-A-5,776,622 has disclosed the use of a if/Al bilayer to enhanced electron injection in organic EL devices.

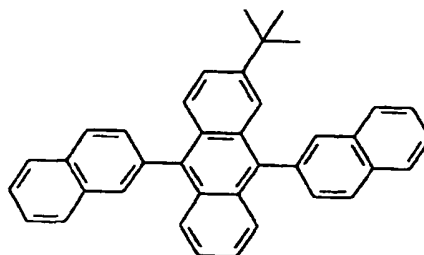
[0020] Conventional anodes 204a are formed of a conductive and transparent oxide. Indium tin oxide has been widely used as the anode contact because of its transparency, good conductivity, and high work function.

[0021] Preferred host materials for the emission layer include:

- a) Alq, and
- b)

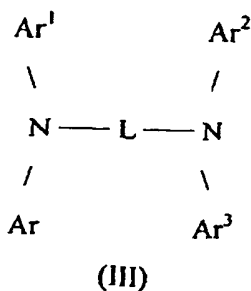


or c)



[0022] Preferred materials for use in forming the electron-transporting layer of the organic EL devices of this invention are metal chelated oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline) as disclosed in US-A-4,885,211. Such compounds exhibit both high levels of performance and are readily fabricated in the form of thin layers.

[0023] The light-transmissive substrate 202 may be constructed of glass, quartz, or a plastic material. Preferred materials for use in forming the hole transport layer of the organic EL devices are tertiary amines as taught in Van Slyke US-A-4,539,507. Another class of preferred amines is tetraaryl amines. Preferred tetraaryldiamines include two diarylamino groups, such as indicated by formula (III), linked through an arylene group. Preferred tetraaryldiamines include those represented by formula (IV).



wherein:

Ar, Ar¹, Ar² and Ar³ are independently selected from among phenyl, biphenyl and naphthyl moieties;
L is a divalent naphthylene moiety or d_n;

d is a phenylene moiety;

n is an integer of from 1 to 4; and

at least one of Ar, Ar¹, Ar² and Ar³ is a naphthyl moiety when L is d_n.

[0024] The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (I), (II), (III), and (IV) can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halogen such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 6 carbon atoms. The cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms, for example cyclopentyl, cyclohexyl, and cycloheptyl ring structures. When the aryl and arylene moieties are not fused aromatic ring moieties, they are preferably phenyl and phenylene moieties.

[0025] Illustrative of useful selected (fused aromatic ring containing) aromatic tertiary amines are the following:

ATA-1 4,4'-Bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB)
ATA-2 4,4''-Bis[N-(1-naphthyl)-N-phenylamino]-p-terphenyl

ATA-3	4,4'-Bis[N-(2-naphthyl)-N-phenylamino]biphenyl
ATA-4	4,4'-Bis[N-(3-acenaphthenyl)-N-phenyl-amino]biphenyl
ATA-5	1,5-Bis[N-(1-naphthyl)-N-phenylamino]naphthalene
ATA-6	4,4'-Bis[N-(9-anthryl)-N-phenylamino]-biphenyl
ATA-7	4,4"-Bis[N-(1-anthryl)-N-phenylamino]-p-terphenyl
ATA-8	4,4'-Bis[N-(2-phenanthryl)-N-phenyl-amino]biphenyl
ATA-9	4,4'-Bis[N-(8-fluoranthryl)-N-phenyl-amino]biphenyl
ATA-10	4,4'-Bis[N-(2-pyrenyl)-N-phenylamino]bi-phenyl
ATA-11	4,4'-Bis[N-(2-naphthacenyl)-N-phenyl-amino]biphenyl
ATA-12	4,4'-Bis[N-(2-perylenyl)-N-phenylamino]biphenyl
ATA-13	4,4'-Bis[N-(1-coroneryl)-N-phenylamino]biphenyl
ATA-14	2,6-Bis(di-p-tolylamino)naphthalene
ATA-15	2,6-Bis[di-(1-naphtyl)amino]naphthalene
ATA-16	2,6-Bis[N-(1-naphthyl)-N-(2-naphthyl)-amino]naphthalene
ATA-17	N,N,N',N'-Tetra(2-naphthyl)-4,4"-di-amino-p-terphenyl
ATA-18	4,4'-Bis[N-phenyl-N-[4-(1-naphthyl)-phenyl]amino]biphenyl
ATA-19	4,4'-Bis[N-phenyl-N-(2-pyrenyl)amino]biphenyl
ATA-20	2,6-Bis[N,N-di(2-naphthyl)amine]fluorene
ATA-21	1,5-Bis[N-(1-naphthyl)-N-phenylamino]naphthalene

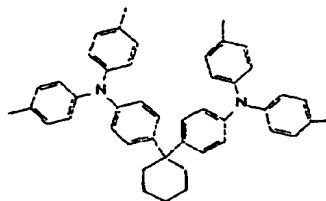
[0026] A preferred embodiment of the luminescent layer consists of a host material doped with fluorescent dyes. Using this method, highly efficient EL devices can be constructed. Simultaneously, the color of the EL devices can be tuned by using fluorescent dyes of different emission wavelengths in a common host material. Tang and others. in commonly assigned US-A-4,769,292 has described this dopant scheme in considerable details for EL devices using Alq as the host material.

[0027] FIG. 3 describes the energy level diagram of the organic emission layer host and the three kinds of dopants used in this invention. This figure refers specifically to an organic emissive layer consisting of a Alq host material and the three dopants: exciton-trapping dopant, hole-trapping dopant, and luminescent dopant.

[0028] A hole trap in Alq, for example, is defined as the dopant which has a bandgap greater than that of Alq, and is capable of donating an electron to Alq. The later condition is satisfied if the highest occupied molecular orbital (HOMO) of the dopant is higher (in electron energy scale) than that of Alq. Experimentally, the HOMO level is measured as the ionization potential with respect to the vacuum level. The ionization potential (IP) of the hole trapping dopant in Alq is determined to be lower than that of the (Alq) host. The IP of Alq is 5.62 eV. The hole trapping dopant, when filled is positively charged.

[0029] Preferred materials for use as a hole trap dopant of the organic EL devices are tetraaryl amines. Some of the arylamines class materials and their ionization potentials are given below.

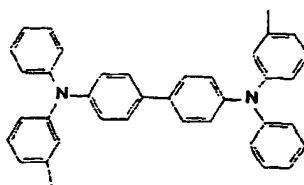
HD1:



HD2:

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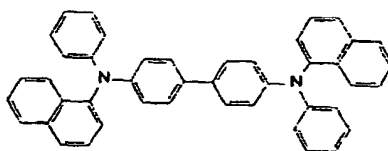


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HD3 (NPB):

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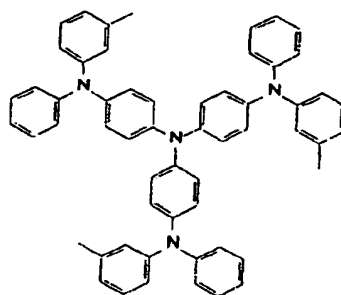


HD4:

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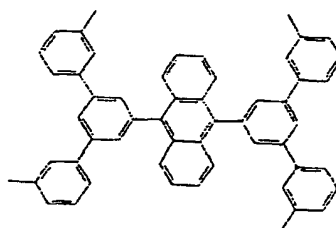
An exciton trap in Alq, for example, is defined as the dopant, which has band gap energy less than that of Alq host material and the trap, when filled, remains electronically neutral.

[0030] Preferred materials for uses as an exciton trap dopant of the organic EL devices are rubrene class materials. Some of the rubrene class materials and their ionization potentials are given below.

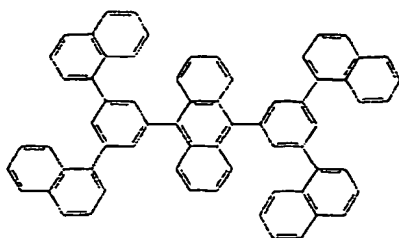
EXD1:

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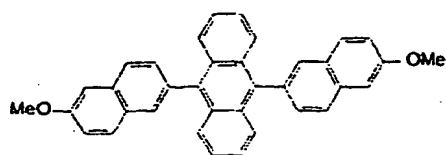
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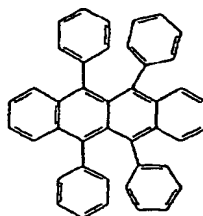
EXD2:



EXD3:



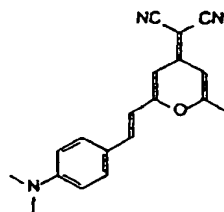
EXD4 (rubrene):



[0031] The luminescent dopant has a bandgap less than the bandgap energy of the first exciton dopant. The exciton dopant is capable of accepting energy from the electron-hole combination in the host material and accepting energy transferred from the second dopant.

[0032] Preferred materials for use as luminescent dopant of the organic EL devices is DCM class materials. Some of the DCJTB structures and their ionization potentials are given below.

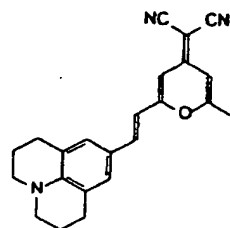
LD1:



LD2:

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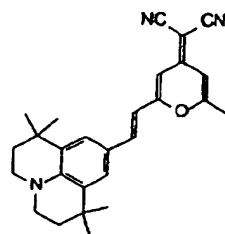


LD3:

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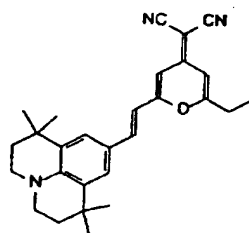


LD4:

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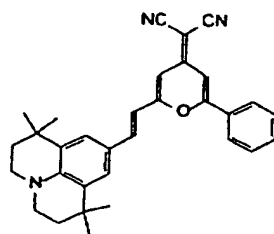


LD5:

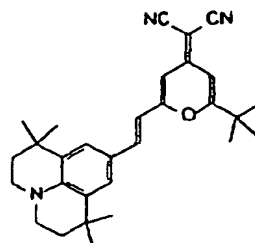
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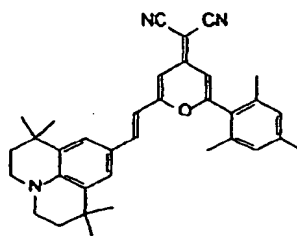
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LD6:



LD7 (DCJTb):



[0033] NPB has been used as a hole-trapping dopant, rubrene as an exciton trapping dopant, and DCJTb as a luminescent dopant into the Alq emission layer as examples illustrating this invention. The energy levels of these materials are shown in FIG. 3.

[0034] Several devices were prepared on the glass substrate using ITO anode and Mg:Ag or LiF/Al cathode in accordance with a device structure as described in FIG. 2. The structure of the device is glass substrate/ITO anode/CFx hole injection layer/ NPB hole transport layer/Alq emission layer with dopant(s)/Alq electron transport layer/Mg:Ag or LiF/Al.

[0035] The ranges of concentration of various dopants in the Alq emission layer used in the EL devices are preferably as follows:

Exciton trapping dopant = 1- 25 %, hole trapping dopant = 0.1 - 35 %, and luminescent dopant = 0.05 - 4%.

[0036] Several devices have been prepared using the above dopants. The results are summarized in Tables 1 and 2.

[0037] Devices prepared doping both exciton dopant and hole trapping dopant have shown significantly higher efficiency and the operational stability as compared to the devices doped with either dopant. Furthermore, the synergetic effect of doping exciton trapping dopant and hole trapping dopant was such that better operational stability and efficiency were obtained. With the addition of third luminescent dopant, excellent color coordinates were obtained with high luminance efficiency, which could not be achieved with any other combination.

[0038] The invention and its advantages are further illustrated by the specific examples which follow. The term "percentage" indicates the volume percentage of a particular dopant with respect to the host material.

Example 1

[0039] An EL device was constructed in the following manner:

[0040] Substrates coated with 80 nm ITO were sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor. These substrates were treated with an oxygen plasma for about one minute and coated with 1 nm fluorocarbon layer by plasma assisted deposition of CHF_3 .

[0041] These substrates were loaded into a deposition chamber for organic layers and cathode depositions.

[0042] Device A was prepared by sequential deposition of 150 nm NPB hole transporting layer, followed by 37.5 nm Alq emission layer without any dopant (EML), 37.5 nm Alq electron transport layer (ETL), then 0.5 nm LiF and 200 nm Al as a part of cathode. The above sequence completed the deposition of the EL device.

[0043] The EL device was then hermetically packaged in a dry glove box filled with nitrogen for protection against ambient environment. The ITO patterned substrates used for preparing these EL devices contained several icons. Each individual icon of the device was tested for current voltage characteristics and the electroluminescence yield.

5 Example 2

[0044] Device B was prepared following the same sequence as Device A except the 37.5 Alq emission layer was doped with 10% rubrene, exciton dopant 1.

10 Example 3

[0045] Device C was prepared following the same sequence as Device A except the 37.5 Alq emission layer was doped with 10% NPB, hole trap dopant 2.

15 Example 4

[0046] Device D was prepared following the same sequence as Device A except the 37.5 Alq emission layer was doped with 5% rubrene and 5% NPB. The deposition rate and thus the volume percentage of the Alq host and the two dopants was controlled by the boat temperature.

20 [0047] The luminance characteristics of these devices are shown in Table 1. The Device A has 3.17 cd/A luminance yield at 20 mA/cm² current density. This device has EL peak position at 532 nm and has green color. When the Alq emission layer was doped with 10% rubrene for Device B, the luminance yield was 4.68 cd/A. The EL peak position was at 568 nm giving yellow emission. When the Alq emission layer was doped with 10% NPB, the luminance yield for Device C increased to 3.27 cd/A @20 mA/cm². The EL peak position is at 528 nm and has green color. When the
25 Alq emission layer was co-doped with 5% rubrene and 5% NPB, the luminance yield for the Device D was 4.95 cd/A and the EL peak position was at 568 nm giving yellow emission.

[0048] The operational stability of the encapsulated devices in ambient environments has been found by measuring the changes in the drive voltage and the luminance as a function of time when four different icons of each of these devices were operated at a constant current density of 20, 40, 60 and 80 mA/cm². The half-life times for these devices
30 are given in Table 1.

Table 1:

Luminance performance of devices A to H with different dopants						
Device	Luminescent layer	Luminance Yield @20 mA/cm ² (cd/A)	EL Peak Wavelength (nm)	CIE _x	CIE _y	Drivevoltage @ 20mA/cm ² (volts)
Device A	Alq	3.17	524	0.334	0.531	8.50
Device B	Alq + 10% Rubrene	4.68	568	0.519	0.476	7.90
Device C	Alq + 10% NPB	3.26	528	0.346	0.538	8.70
Device D	Alq + 5% Rubrene + 5% NPB	4.95	568	0.518	0.478	8.30
Device E	Alq + 2% DCJT-B	2.05	628	0.640	0.355	9.20
Device F	Alq + 2% DCJT-B + 10% Rubrene	2.41	632	0.650	0.345	9.00
Device G	Alq + 2% DCJT-B + 10% NPB	2.08	628	0.645	0.353	9.10
Device H	Alq + 2% DCJT-B + 5% NPB + 5% Rubrene	2.76	632	0.650	0.350	8.50

[0049] FIG. 4 shows the normalized luminance as a function of operating time at 20mA/cm² current density for the four Devices A to D. The synergetic effect of doping exciton trapping dopant and hole trapping dopant was found with

doping simultaneously with NPB and rubrene into Alq host. The decrease in luminance yield for Device D was the lowest as compared to the Devices A, B, and C. The change in luminance was unexpectedly lower than that possible from the additive effects of both dopants. The synergetic effect was such that better operational stability and efficiency were obtained at lower concentrations of the dopants. This resulted in more than two times improvement in operating lifetime and 10-20% increase in luminance efficiency, which could not be achieved with using either of the dopants with any amounts of doping concentrations.

[0050] FIG. 5 shows the operational stability of the drive voltage at 20mA/cm² current density. Unexpectedly, again the Device D with the Alq emission layer doped with both rubrene and NPB dopants showed minimal change in the drive voltage. Thus, Device D has the highest operational stability among the four devices. Thus, the normalized luminance and the drive voltage was stable for a longer time for the devices of this invention.

Examples 5 - 8:

[0051] In accordance with the method described for Devices A-D, except that the dopants in the 37.5 nm Alq emission layer.

Example 5

[0052] For Device E, the 37.5 nm Alq emission layer contained 2% DCJTB luminescent dopant.

Example 6

[0053] For Device F, the 37.5 nm Alq emission layer contained 2% DCJTB luminescent dopant and 10% rubrene exciton dopant.

Example 7

[0054] For Device G, the 37.5 nm Alq emission layer contained 2% DCJTB luminescent dopant and 10% NPB hole trapping dopant.

Example 8

[0055] For Device H, the 37.5 nm Alq emission layer contained three dopants, 2% DCJTB + 5% rubrene + 5% NPB.

[0056] The luminance characteristics of these are included in Table 1. The Device E has 2.05 cd/A luminance yield at 20 mA/cm² current density. This device has EL peak position at 628 nm and has red color having color coordinates CIE_x = 0.64 and CIE_y = 0.35. When the Alq emission layer was doped with 2% DCJTB + 10% rubrene, the luminance yield for Device F increased to 2.41 cd/A @20 mA/cm². The EL peak position is at 628 nm and has red color having color coordinates CIE_x = 0.64 and CIE_y = 0.34. When the Alq emission layer was doped with 2% DCJTB + 10% NPB for Device G, the luminance yield was 2.06 cd/A. The EL peak position was at 628 nm giving red emission at 628 nm and color coordinates CIE_x = 0.64 and CIE_y = 0.34. When the Alq emission layer was co-doped three dopants, 2% DCJTB + 5% rubrene + 5% NPB, the luminance yield for the Device H was 2.76 cd/A and the EL peak position was at 628 nm giving red emission at 628 nm and color coordinates of CIE_x = 0.65 and CIE_y = 0.34. The drive voltage at 20 mA/cm² current density was lowest for the Device H. Thus the Device H prepared with the Alq host emission layer doped with three dopants: DCJTB luminescent dopant; rubrene exciton dopant and NPB hole trap dopant have higher luminance efficiency; lowest drive voltage and excellent color coordinates.

[0057] The operational stability of these encapsulated devices has been found by measuring the changes in the luminance and the drive voltage as a function of time. Again four icons of each device was operated at the current density of 20, 40, 60 and 80 20 mA/cm². The half-life times for these devices are included in Table 2.

Table 2:

Operational Half-life times of devices A to H with different dopants					
Device	Luminescent layer	Half life @J=80 mA/cm ² (Hours)	Half life @J=60 mA/cm ² (Hours)	Half life @J=40 mA/cm ² (Hours)	Half life @J=20 mA/cm ² (Hours)
Device A	Alq	156	161	38	1000
Device B	Alq + 10% Rubrene	455	542	1103	3000

Table 2: (continued)

Operational Half-life times of devices A to H with different dopants					
Device	Luminescent layer	Half life @J=80 mA/cm ² (Hours)	Half life @J=60 mA/cm ² (Hours)	Half life @J=40 mA/cm ² (Hours)	Half life @J=20 mA/cm ² (Hours)
Device C	Alq + 10% NPB	348	525	1025	3250
Device D	Alq + 5% Rubrene + 5% NPB	900	1300	2200	5000
Device E	Alq + 2% DCJT-B	361	510	901	2250
Device F	Alq + 2% DCJT-B + 10% Rubrene	487	710	1482	3500
Device G	Alq + 2% DCJT-B + 10% NPB	563	822	1557	4000
Device H	Alq + 2% DCJT-B + 5% NPB + 5% Rubrene	901	1353	2250	>6000

[0058] FIG. 6 shows the operational luminance stability of the four Devices E to H. It is obvious that Device H prepared with all the three dopants, 2% DCJT-B + 5% NPB + 5% rubrene into the Alq host layer has the highest operational stability. This device also has the best color coordinates and the highest luminance efficiency and lowest drive voltage.

[0059] FIG. 7 shows the operational voltage stability of the above four Devices E to H. Again, the Device H prepared with all the three dopants, 2% DCJT-B + 5% NPB + 5% rubrene in Alq host layer has minimal increase in the drive voltage over the operational time and thus the highest operational voltage stability.

[0060] With the addition of third luminescent dopant, such as DCJT-B, excellent red emission color coordinates were obtained with high luminance efficiency and lowest drive voltage, which could not be achieved with any other combination.

[0061] Thus the EL devices of this invention prepared with Alq emission containing rubrene and NPB with or without DCJT-B luminescent dopant have significantly improved operational fade stability. These devices have higher luminance yield and lower drive voltage. These devices can be operated at higher current density with minimum degradation in the color coordinates and the luminance efficiency. The devices with the emission layer containing all the three dopants, rubrene exciton trap, NPB hole trap and DCJT-B luminescent dopant, have the highest luminance yield, lowest drive voltage, best chromaticity and the highest operational stability.

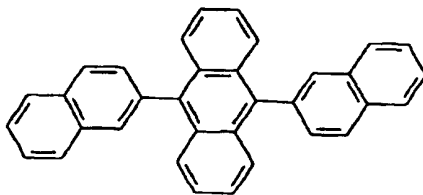
[0062] Other features of the invention are included below.

[0063] The organic luminescent layer wherein concentration of the second dopant is in a range of 0.5% to 25% by volume of the organic luminescent layer.

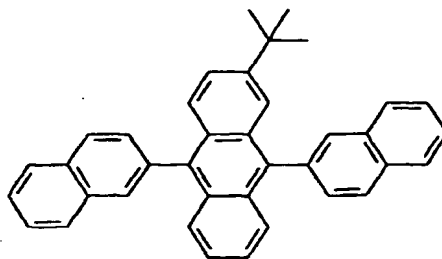
[0064] The organic luminescent layer wherein the host material includes:

a) Alq; and

b)



or c)

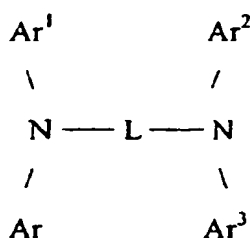


[0065] The organic luminescent layer wherein the first dopant includes a fluorescent hydrocarbon compound containing a polycyclic benzoid chromophoric unit.

[0066] The organic luminescent layer wherein the second dopant includes aromatic tertiary amines.

[0067] The organic luminescent layer wherein the aromatic tertiary amines are tetraaryldiamines.

[0068] The organic luminescent layer wherein the aromatic tertiary amines include tetraaryldiamines having the formula:



wherein:

Ar, Ar¹, Ar² and Ar³ are independently selected from among phenyl, biphenyl and naphthyl moieties;

L is a divalent naphthylene moiety or d_n;

d is a phenylene moiety;

n is an integer of from 1 to 4, and

at least one of Ar, Ar¹, Ar² and Ar³ is a naphthyl moiety when L is d_n.

[0069] The organic luminescent layer wherein the third dopant includes DCM class of materials.

[0070] The organic luminescent layer wherein the third dopant includes DCJTb.

[0071] The organic luminescent layer wherein concentration of the first dopant is in a range of 0.5% to 25% by volume of the organic luminescent layer

[0072] The organic luminescent layer wherein concentration of the second dopant is in a range of 0.5% to 25% by volume of the organic luminescent layer

[0073] The organic luminescent layer wherein concentration of the third dopant is greater than 0.05% and less than 5% by volume of the organic luminescent layer.

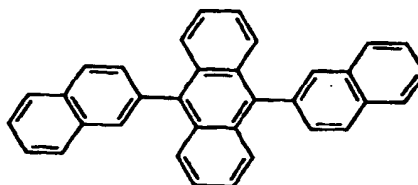
[0074] The organic luminescent layer wherein the combined concentration of the first, second, and third dopants is greater than 1.05% and less than 55% by volume of the organic luminescent layer.

Claims

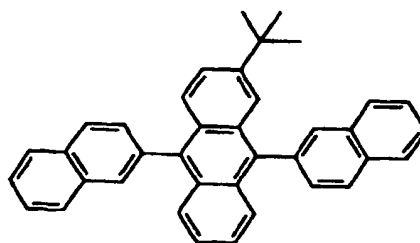
1. An organic luminescent layer for use in an electroluminescent device with improved operating life, comprising:

a) an organic host material capable of sustaining both hole and electron injection and recombination wherein

the host material includes Alq; and



or



and

b) at least three dopants:

- i) a first dopant capable of accepting energy of electron hole combination in the host material;
- ii) a second dopant capable of trapping the holes from the host material; and
- iii) a third dopant capable of accepting energy from the electron hole combination in the host material and accepting energy transferred from the second dopant;

c) the first dopant being selected so that the bandgap energy of the first dopant is less than the bandgap energy of the host material; and

d) the second dopant being selected to have a hole trapping energy level above the valence band of the host material; and

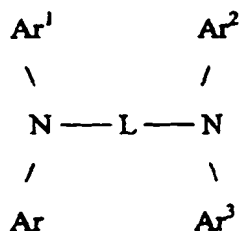
e) the third dopant having a bandgap energy less than the bandgap energy of the first dopant.

2. The organic luminescent layer of claim 1 wherein the first dopant includes a fluorescent hydrocarbon compound containing a polycyclic benzoid chromophoric unit.

3. The organic luminescent layer of claim 1 wherein the second dopant includes aromatic tertiary amines.

4. The organic luminescent layer of claim 3 wherein the aromatic tertiary amines are tetraaryldiamines.

5. The organic luminescent layer of claim 4 wherein the aromatic tertiary amines include tetraaryldiamines having the formula:



wherein:

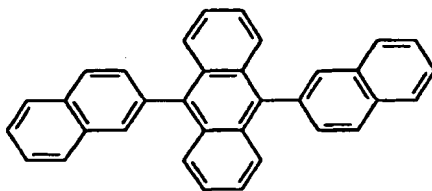
Ar, Ar¹, Ar² and Ar³ are independently selected from among phenyl, biphenyl and naphthyl moieties;
 L is a divalent naphthylene moiety or d_n;
 d is a phenylene moiety;
 n is an integer of from 1 to 4, and
 at least one of Ar, Ar¹, Ar² and Ar³ is a naphthyl moiety when L is d_n.

6. The organic luminescent layer of claim 1 wherein the third dopant includes DCM class of materials.
7. The organic luminescent layer of claim 1 wherein the third dopant includes DCJTb.
8. The organic luminescent layer of claim 1 wherein concentration of the first dopant is in a range of 0.5% to 25% by volume of the organic luminescent layer.
9. The organic luminescent layer of claim 1 wherein concentration of the second dopant is in a range of 0.5% to 25% by volume of the organic luminescent layer.
10. The organic luminescent layer of claim 1 wherein concentration of the third dopant is greater than 0.05% and less than 5% by volume of the organic luminescent layer.
11. The organic luminescent layer of claim 1 wherein the combined concentration of the first, second, and third dopants is greater than 1.05% and less than 55% by volume of the organic luminescent layer.

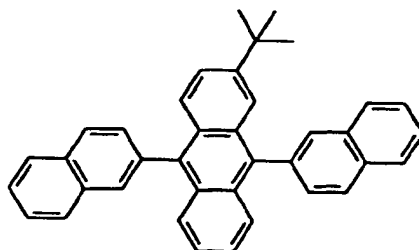
Patentansprüche

1. Organische Lumineszenzschicht zur Verwendung in einer Elektrolumineszenzvorrichtung mit verbesserter Betriebsdauer, die folgendes umfasst:

a) ein organisches Wirtsmaterial, das eine Loch- und Elektroneninjektion und -Rekombination zu überdauern vermag, worin das Wirtsmaterial Alq umfasst; und



oder



und

b) mindestens drei Dotierungen:

i) eine erste Dotierung, die in der Lage ist, Energie einer Elektronenlochkombination im Wirtsmaterial aufzunehmen;

ii) eine zweite Dotierung, die in der Lage ist, Löcher von dem Wirtsmaterial einzufangen; und

iii) eine dritte Dotierung, die in der Lage ist, Energie aus der Elektronenlochkombination im Wirtsmaterial aufzunehmen und aus der zweiten Dotierung übertragene Energie aufzunehmen;

c) wobei die erste Dotierung derart gewählt ist, dass die Energielücke der ersten Dotierung kleiner als die Energielücke des Wirtsmaterials ist; und

d) wobei die zweite Dotierung derart gewählt ist, dass sie eine Locheinfang-Energieschwelle oberhalb des Valenzbandes des Wirtsmaterials aufweist; und

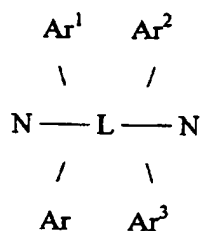
e) wobei die dritte Dotierung eine Energielücke aufweist, die kleiner als die Energielücke der ersten Dotierung ist.

2. Organische Lumineszenzschicht nach Anspruch 1, worin die erste Dotierung eine fluoreszierende Kohlenwasserstoffverbindung umfasst, die eine polyzyklische, benzoide, chromophore Einheit enthält.

3. Organische Lumineszenzschicht nach Anspruch 1, worin die zweite Dotierung aromatische, tertiäre Amine umfasst.

4. Organische Lumineszenzschicht nach Anspruch 3, worin die aromatischen, tertiären Amine Tetraaryldiamine sind.

5. Organische Lumineszenzschicht nach Anspruch 4, worin die aromatischen, tertiären Amine Tetraaryldiamine mit folgender Formel enthalten:



worin:

Ar, Ar¹, Ar² und Ar³ sind aus Phenyl-, Biphenyl- und Naphthylresten unabhängig wählbar sind;

L für einen zweiwertigen Naphthylrest oder für d_n steht;

d für einen Phenylrest steht;

n für eine Zahl von 1 bis 4 steht; und

mindestens Ar, Ar¹, Ar² oder Ar³ für einen Naphthylrest steht, wenn L für d_n steht.

6. Organische Lumineszenzschicht nach Anspruch 1, worin die dritte Dotierung Materialien der DCM-Klasse umfasst.

7. Organische Lumineszenzschicht nach Anspruch 1, worin die dritte Dotierung DCJTb umfasst.

8. Organische Lumineszenzschicht nach Anspruch 1, worin die Konzentration der ersten Dotierung in einem Bereich von 0,5 Vol.-% bis 25 Vol.-% der organischen Lumineszenzschicht liegt.

9. Organische Lumineszenzschicht nach Anspruch 1, worin die Konzentration der zweiten Dotierung in einem Bereich von 0,5 Vol.-% bis 25 Vol.-% der organischen Lumineszenzschicht liegt.

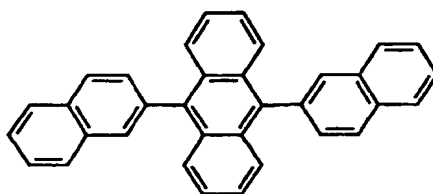
10. Organische Lumineszenzschicht nach Anspruch 1, worin die Konzentration der dritten Dotierung größer als 0,05 Vol.-% und kleiner als 5 Vol.-% der organischen Lumineszenzschicht ist.

11. Organische Lumineszenzschicht nach Anspruch 1, worin die kombinierte Konzentration der ersten, zweiten und dritten Dotierung größer als 1,05 Vol.-% und kleiner als 55 Vol.-% der organischen Lumineszenzschicht ist.

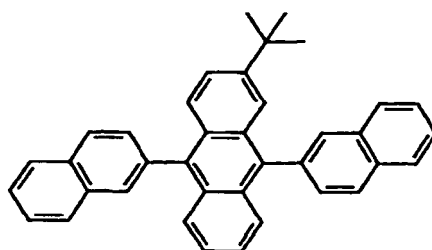
Revendications

1. Couche organique luminescente destinée à être utilisée dans un dispositif électroluminescent ayant une durée de vie améliorée, comprenant :

a) un matériau organique hôte capable de supporter une injection et une recombinaison de trous et d'électrons, dans lequel le matériau hôte contient Alq ; et



ou



et

b) au moins trois dopants :

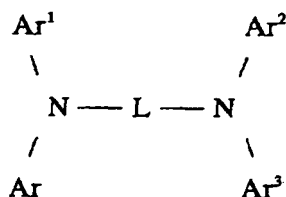
- i) un premier dopant capable d'accepter l'énergie produite par la combinaison électron-trou dans le matériau hôte ;
- ii) un second dopant capable de piéger les trous du matériau hôte ; et
- iii) un troisième dopant capable d'accepter l'énergie produite par la combinaison électron-trou dans le matériau hôte et d'accepter l'énergie transférée par le second dopant ;

c) le premier dopant étant choisi de telle sorte que l'énergie de la largeur de bande interdite du premier dopant est inférieure à l'énergie de la largeur de bande interdite du matériau hôte ; et

d) le second dopant étant choisi de manière à avoir un niveau d'énergie de piégeage de trous supérieur à la bande de valence du matériau hôte ; et

e) le troisième dopant ayant une énergie de largeur de bande interdite inférieure à l'énergie de largeur de bande interdite du premier dopant.

2. Couche organique luminescente selon la revendication 1, dans laquelle le premier dopant contient un composé d'hydrocarbure fluorescent contenant une unité chromophore de type benzoïde polycyclique.
3. Couche organique luminescente selon la revendication 1, dans laquelle le second dopant contient des amines tertiaires aromatiques.
4. Couche organique luminescente selon la revendication 3, dans laquelle les amines tertiaires aromatiques sont des tétraaryldiamines.
5. Couche organique luminescente selon la revendication 4, dans laquelle les amines tertiaires aromatiques comprennent des tétraaryldiamines ayant la formule :



dans laquelle :

- Ar, Ar¹, Ar² et Ar³ sont choisis séparément parmi les groupes phényle, biphényle et naphthyle ;
- L est un groupe naphthylène divalent ou d_n ;
- d est un groupe phénylène ;
- n est un nombre entier de 1 à 4 ; et
- au moins l'un des groupes Ar, Ar¹, Ar² et Ar³ est un groupe naphthyle lorsque L représente d_n.

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6. Couche organique luminescente selon la revendication 1, dans laquelle le troisième dopant comprend la classe DCM de matériaux.
7. Couche organique luminescente selon la revendication 1, dans laquelle le troisième dopant contient DCJTb.
8. Couche organique luminescente selon la revendication 1, dans laquelle la concentration du premier dopant est comprise entre 0,5 % et 25 % en volume de la couche organique luminescente.
9. Couche organique luminescente selon la revendication 1, dans laquelle la concentration du second dopant est comprise entre 0,5 % et 25 % en volume de la couche organique luminescente.
10. Couche organique luminescente selon la revendication 1, dans laquelle la concentration du troisième dopant est supérieure à 0,05 % et inférieure à 5 % en volume de la couche organique luminescente.
11. Couche organique luminescente selon la revendication 1, dans laquelle la concentration combinée des premier, second et troisième dopants est supérieure à 1,05 % et inférieure à 55 % en volume de la couche organique luminescente.

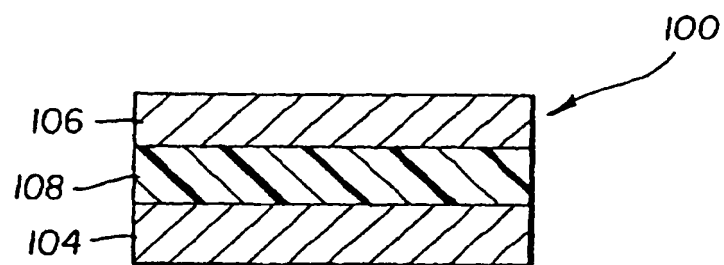


FIG. 1

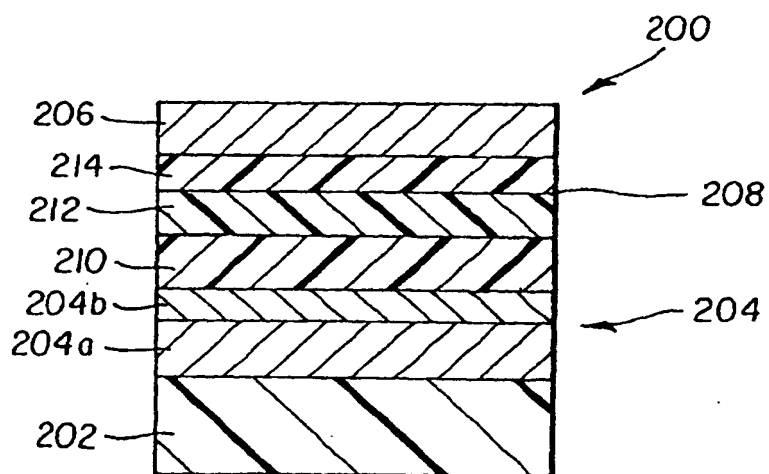


FIG. 2

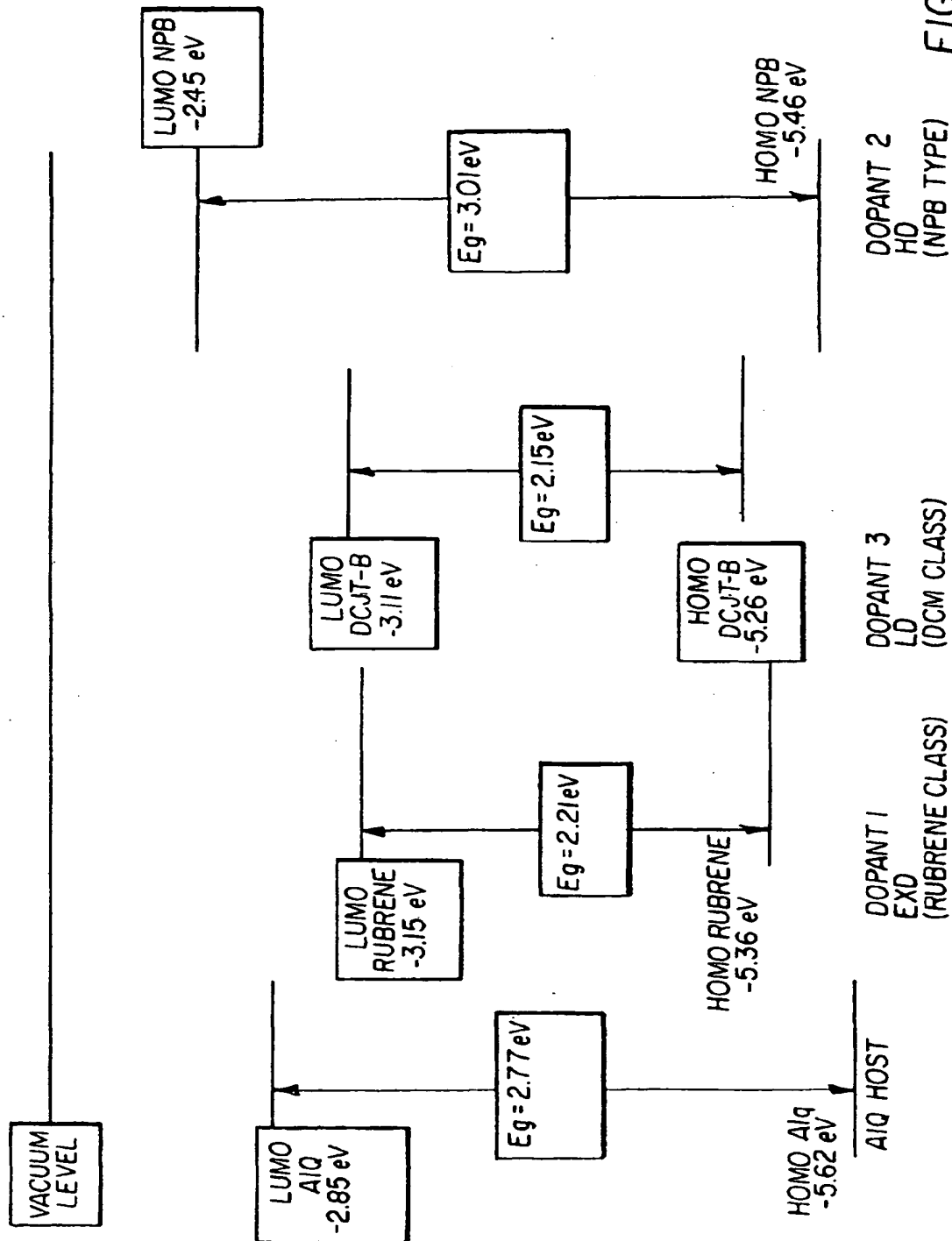


FIG. 3

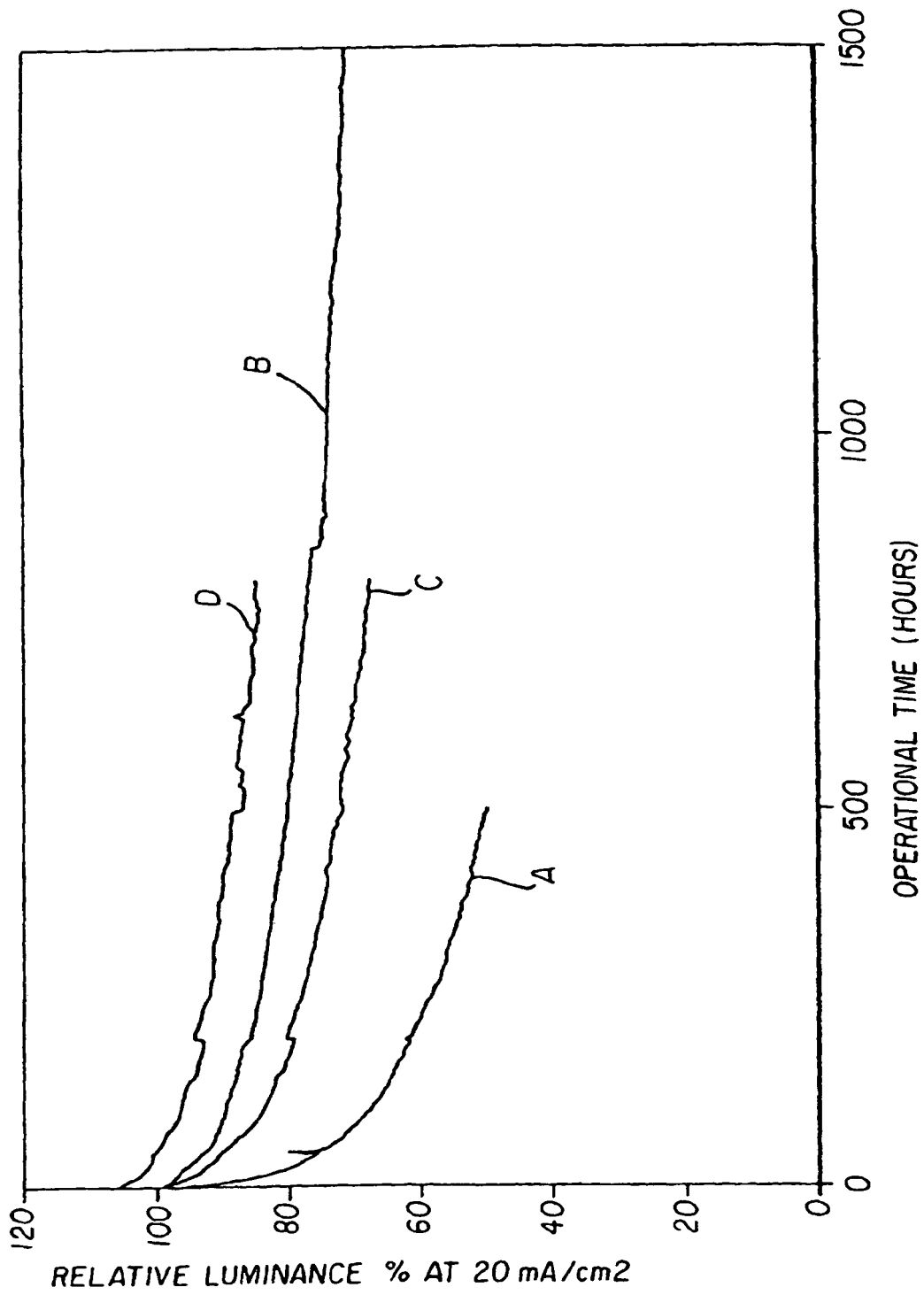


FIG. 4

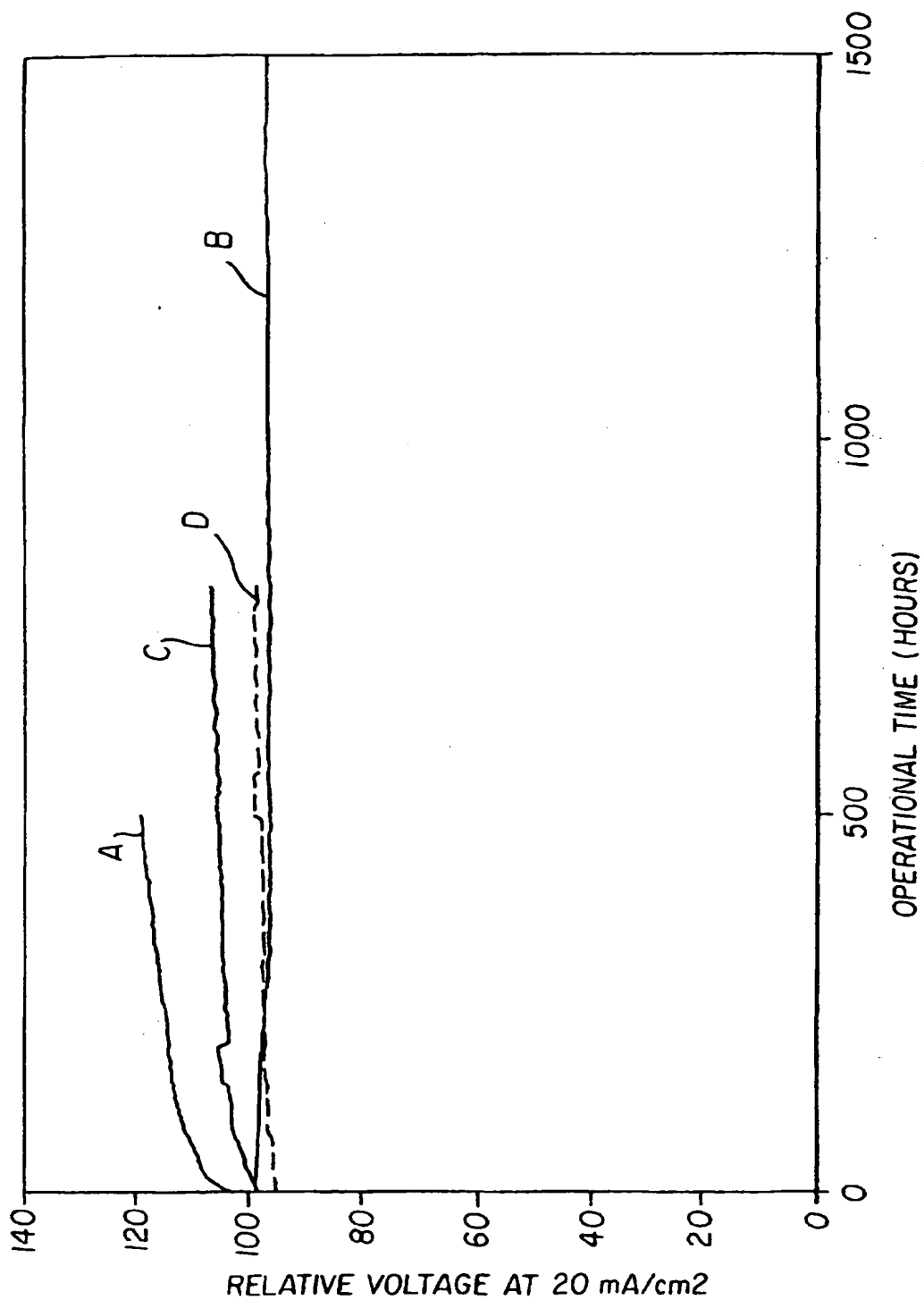


FIG. 5

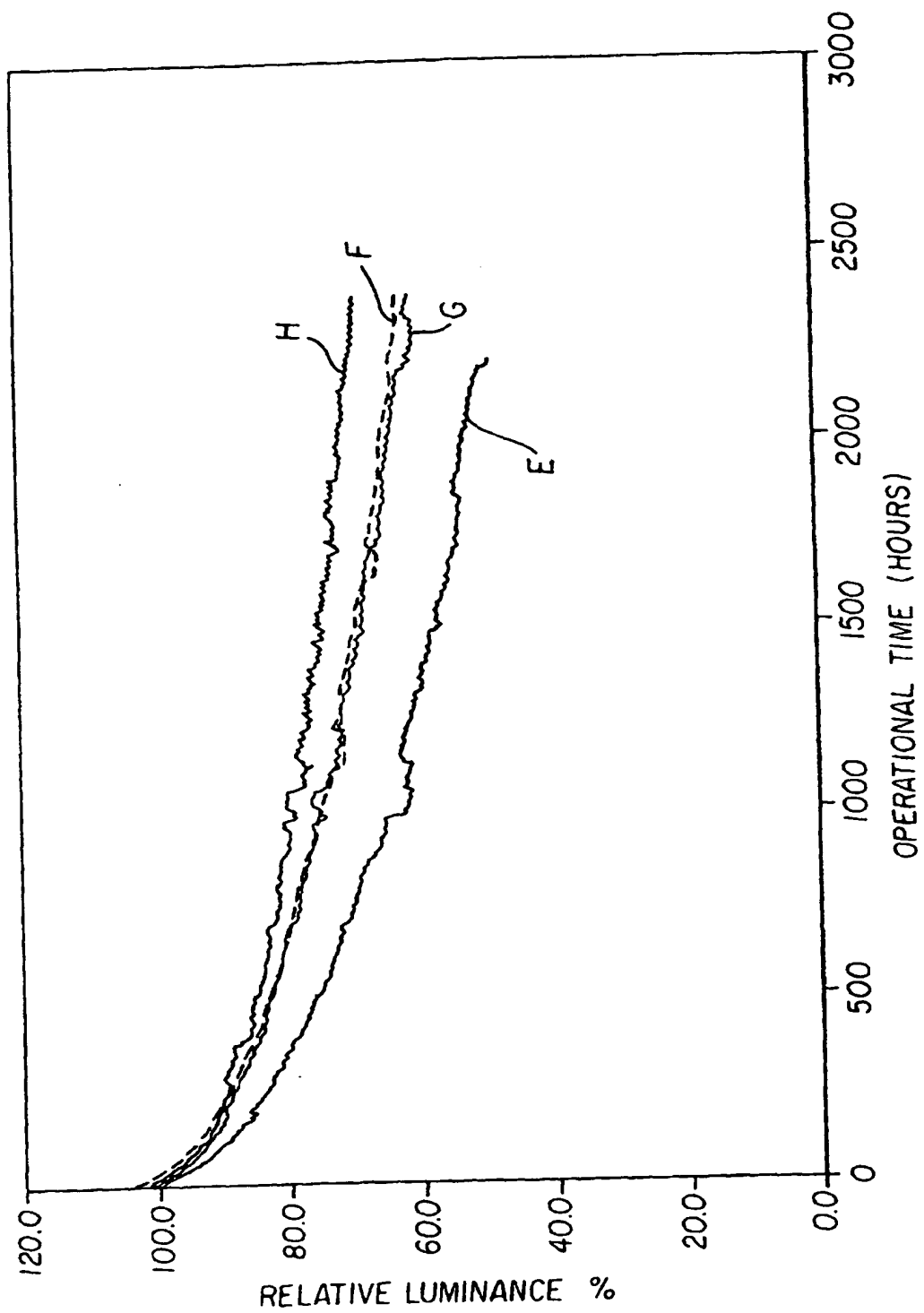


FIG. 6

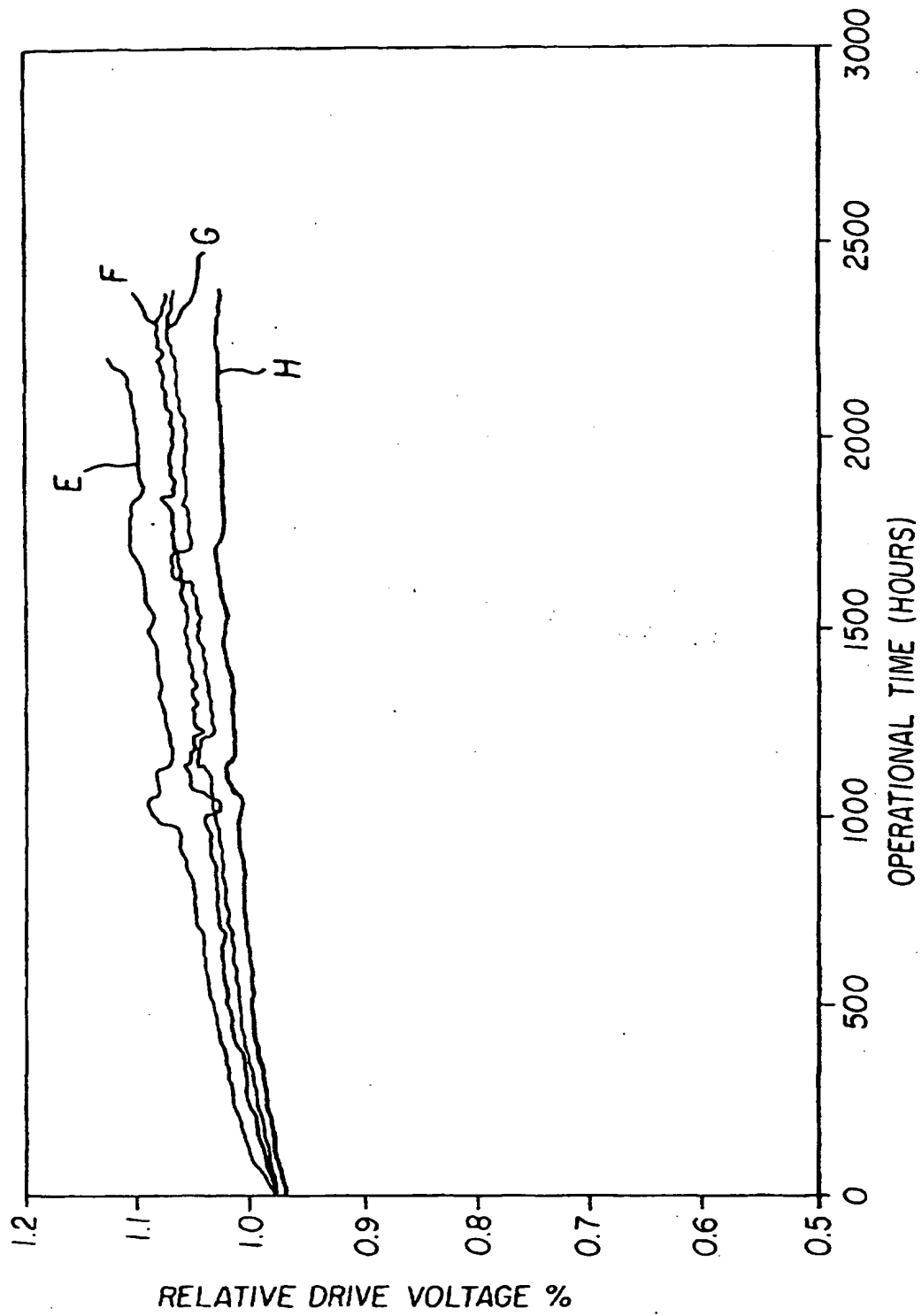


FIG. 7

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